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(54) **Hot melt adhesive compositions.**

(57) This invention relates to hot melt adhesive compositions which include a highly unsaturated hydrocarbon rubber or neoprene, about 5 to about 100 parts by weight of neutralised sulphonated EPDM terpolymer per 100 parts by weight of the highly usaturated hydrocarbon rubber or neoprene, wherein the neutralised sulphonated EPDM terpolymer has about 5 to about 50 meq. of neutralised sulphonate groups per 100 grams of the neutralised sulphonated EPDM terpolymer, and about 25 to about 200 parts by weight of a hydrocarbon resin derived from polymerisation of petroleum or coal distillates consisting of dienes, mono- and di-olefins and cyclic olefins having 5 or 6 carbon atoms per 100 parts by weight of the highly unsaturated hydrocarbon rubber or neoprene.

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HOT MELT ADHESIVE COMPOSITIONS

This invention relates to hot melt adhesive compositions which include a highly unsaturated hydrocarbon rubber, 5 to 100 parts by weight of a neutralized sulfonated EPDM-ter-polymer per 100 parts by weight of the highly unsaturated hydrocarbon rubber, wherein the neutralized sulfonated EPDM ter-polymer has 5 to 50 meq. of neutralized sulfonate groups per 100 grams of the neutralized sulfonated elastomeric polymer, and about 25 to 200 parts by weight of a hydrocarbon resin of a petroleum or coal tar distillate, having 5 to 6 carbon atoms the hydrocarbon resin being composed of aliphatic dienes and monoolefins per 100 parts by weight of the highly unsaturated hydrocarbon rubber.

Several U.S. Patents have described sulfonated polymers such as sulfonated butyl and sulfonated EPDM in adhesive applications (e.g. U.S. 3,867,247 and U.S. 3,801,531). It is important to distinguish the present invention over those prior art systems. The former patent is directed at a sulfonated butyl cement which is solvent based and is employed to laminate various substrates. It is important to note that the present invention differs dramatically from that patent as follows:

(a) The adhesives of the present invention are not deposited from solvents but are hot melt and require no solvents.

(b) The adhesives of the present invention incorporate substantial levels of a highly unsaturated hydrocarbon rubber which is a critical component of these systems.

(c) The present invention may optionally include a preferential plasticizer capable of associating with the metal sulfonate groups and thereby reducing the melt viscosity of the resulting blends to make the systems more processable.

(d) The present invention is directed at sulfonated EPDM, whereas most of the prior art deals with sulfonated butyl rubber (e.g. U.S. 3,867,247).

With regard to the latter point, historically EPDM systems do not possess good tack properties and substantial art exists directed towards improving the adhesive characteristics of such systems. This problem becomes even more acute when EPDM is sulfonated to levels of 5 to 50 milliequivalents (meq.) per 100 grams of polymer and neutralized. The resulting compositions have been widely used as the basis for thermoplastics elastomers (i.e. U.S. patent 4,157,922; 4,014,831; etc.). The use of these materials in such applications is, in part, a demonstration that the properties of such materials are just the opposite of those desired for adhesive. In fact such materials are remarkably devoid of tack or adhesion. The tack, therefore, of converting such physically crosslinked materials into suitable adhesive candidates is a particularly challenging one for two reasons: (a) the EPDM backbone is particularly unsuited for that purpose being a very dry elastomer; (b) the strong associations attributable to metal sulfonate crosslinks further inhibit adhesion to any particular substrate.

Despite these handicaps there are some very good reasons for solving the problems associated with converting sulfonated EPDM into a good hot melt adhesive composition. The excellent thermal stability inherent in the EPDM backbone is a very desirable property for adhesives which will be exposed to high temperatures for long times. Most adhesives based on other elastomeric backbones can suffer degradation under those conditions.

The present invention relates to unique and novel hot melt adhesive compositions which comprise a blend of a highly unsaturated hydrocarbon rubber, a neutralized sulfonated elastomeric polymer which is preferably an EPDM terpolymer, and a hydrocarbon resin, wherein to the

compositions can be optionally added an ionic preferential plasticizer oil, and/or a filler thereby modifying the rheological and physical properties of the hot melt adhesive compositions.

A. Hydrocarbon Rubber

The highly unsaturated hydrocarbon elastomers are polyisoprene, polybutadiene, polypentenamer, natural rubber, styrene-butadiene rubber, styrene/butadiene and styrene/isoprene block copolymers or mixtures thereof. Also possible is neoprene (polychloroprene). Polyisoprene and natural rubber are the preferred members of this group.

An excellent description of various types of isoprene polymers is found in the "Encyclopedia of Polymer Science and Technology", Vol. 7, page 782, Interscience Publishers, Div. of J. Wiley & Sons 1967 edition. The polyisoprenes useful in the present invention vary in structure and can be primarily cis 1,4 polyisoprene or primarily trans 1,4 polyisoprene. It is preferred that these material should not be highly crystalline; it is preferred that they possess little or no crystallinity in order that they impart a suitable level of tack to the blends herein described.

Polyisoprene can vary widely in molecular weight, resulting in a significant difference in physical properties of the polymer and its blends. The use of low molecular weight polyisoprenes gives rise to a tacky product when incorporated in the blends of the present invention, while physical properties of such blends such as peel strength can suffer. The use of very high molecular weight polyisoprenes, however, can provide a more stringent control over the levels and types of other polymers or tackifiers incorporated in the blends due to some decrease in compatibility. However, such high molecular weight polyisoprenes can result in desirably high peel strengths. Generally, one uses polyisoprenes which vary in number average molecular weight from 4,000 to 500,000, preferably from 10,000 to 400,000.

Similarly, the other highly unsaturated polymers such as natural rubber can be employed over a range of molecular weights. Obviously in the case of natural rubber, the range of available molecular weights is more limited than in the case of the synthetic polyisoprenes, nevertheless, those polymers which are commercially available are satisfactory in the present invention. In those cases where a lower molecular weight elastomer is desired, it can be achieved by shear on a rubber mill which is a well-known technique to lower the molecular weight.

B. Sulfonated Polymer and Process for Forming

The neutralized sulfonated elastomeric polymers of this present invention are derived from unsaturated EPDM terpolymers.

EPDM polymers are known in the rubber industry as very dry rubbers meaning that they are relatively non-tacky, and indeed are very limited in adhesive applications for that reason. Therefore, the present invention is specifically attractive for sulfonated EPDM systems in that these materials possess a very high degree of ionic crosslinking which can be controlled by plasticization yet can be modified with the blends taught herein to have good adhesive qualities. This combination of good adhesion and adequate tensile properties is highly sought in a number of adhesive applications, yet is particularly difficult to achieve with the sulfonated ethylene propylene terpolymers. This invention will describe how such elastomers can be blended to achieve some of these desirable properties.

The EPDM terpolymers are low unsaturation polymers having 1 to 10.0, more preferably 2 to 8, most preferably 3 to 7 wt.% olefinic unsaturation defined according to the definition as found in ASTM D-1418-64 and is intended to mean terpolymers containing ethylene and propylene in the backbone and a diene in the side chain. Illustrative methods for producing

these terpolymers are found in U.S. Patent 3,280,082; British Patent 1,030,289 and French Patent 1,386,600. The preferred polymers contain 40 to 65 wt.% ethylene and about 1 to about 10 wt. % of a diene monomer, the balance of the polymer being propylene. Preferably, the polymer contains 45 to 65 wt.% more preferably 45 to 60 wt. %, e.g., 50 wt. % ethylene and 2.6 to 8.0 wt.%, e.g. 5.0 wt.% diene monomer. Such EPDM polymers are substantially noncrystalline meaning they possess less than 20% crystallinity as determined by x-ray techniques. The diene monomer is preferably a non-conjugated diene. Illustrative of these non-conjugated diene monomers which may be used in the terpolymer (EPDM) are 1,4-hexadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-methylene-2-norbornene, 5-propenyl-2-norbornene, and methyl tetrahydroindene. A typical EPDM is Vistalon 2504 (Exxon Chemical Co.), a terpolymer having a Mooney viscosity (ML, 1 + 8, 212°F) of 40 and having an ethylene content of 50 wt. % and a 5-ethylidene-2-norbornene content of 5.0 wt. %. The $\bar{M}n$ as measured by GPC of Vistalon 2504 is 47,000, the $\bar{M}v$ as measured by GPC is 145,000 and the $\bar{M}w$ as measured by GPC is 174,000. Another EPDM terpolymer Vistalon 2504-20 is derived from Vistalon 2504 (Exxon Chemical Co.) by a controlled extrusion process, wherein the resultant Mooney viscosity (ML, 1 + 8, 212°F) is 20. The $\bar{M}n$ as measured by GPC of Vistalon 2504-20 is 26,000, the $\bar{M}v$ as measured by GPC is 90,000 and the $\bar{M}w$ as measured by GPC is about 125,000. Nordel 1320 (DuPont) is another terpolymer having a Mooney viscosity (ML, 1 + 8, 212°F) of 25 and having 53 wt. % of ethylene, 3.5 wt. % of 1,4-hexadiene, and 43.5 wt. % of propylene.

Another EPDM terpolymer Vistalon (MD-76-5) is a terpolymer having a Mooney viscosity (ML, 1 + 8, 212°F) of 20, and $\bar{M}n$ as measured by GPC of 60,000 and a

wt. % ethylene content of 55.

The EPDM terpolymers of this invention have a number average molecular weight ($\bar{M}n$) as measured by GPC of about 10,000 to 200,000, more preferably of 15,000 to 15,000 to 100,000, and most preferably of 20,000 to 60,000. The Mooney viscosity (ML, 1 + 8, 212°F) of the EPDM terpolymer is 5 to 50, more preferably 10 to 50, most preferably 10 to 40. The $\bar{M}v$ as measured by GPC of the EPDM terpolymer is preferably below 350,000 and more preferably below 300,000. The $\bar{M}w$ as measured by GPC of the EPDM terpolymer is preferably below 500,000 and more preferably below 350,000.

The sulfonated EPDM terpolymers are formed by dissolving the elastomeric polymer in a non-reactive solvent such as chlorinated aliphatic solvent, chlorinated aromatic hydrocarbon, an aromatic hydrocarbon, or an aliphatic hydrocarbon such as carbon tetrachloride, dichloroethane, chlorobenzene, benzene, toluene, xylene, cyclohexane, pentane, isopentane, hexane, isohexane or heptane. The preferred solvents are the lower boiling aliphatic hydrocarbons. A sulfonating agent is added to the solution of the elastomeric polymer and non-reactive solvent at a temperature of -100°C to 100°C for a period of time of 1 to 60 minutes, most preferably at room temperature for 5 to 45 minutes; and most preferably 15 to 30. Typical sulfonating agents are described in U.S. Patents 3,642,728 and 3,836,511. The sulfonating agents are selected from an acyl sulfate, a mixture of sulfuric acid and an acid anhydride or a complex of a sulfur trioxide donor and a Lewis base containing oxygen, sulfur, or phosphorus. Typical sulfur trioxide donors are SO_3, chlorosulfonic acid, fluorosulfonic acid, sulfuric acid, oleum, etc. Typical Lewis bases are: dioxane, tetrahydrofuran tetrahydrothiophene or triethyl phosphate. The most

preferred sulfonation agent for this invention is one of the acyl sulfates benzoyl, acetyl, propionyl or butyryl sulfate. The acyl sulfate can be formed in situ in the reaction medium or pre-generated before its addition to the reaction medium in a chlorinated aliphatic or aromatic hydrocarbon.

It should be pointed out that neither the sulfonating agent nor the manner of sulfonation is critical, provided that the sulfonating method does not degrade the EPDM terpolymer backbone. The reaction is quenched with an aliphatic alcohol such as methanol, ethanol or isopropanol, with an aromatic hydroxyl compound, such as phenol, as cycloaliphatic alcohol such as cyclohexanol or with water. The sulfonated EPDM terpolymer has about 5 to about 50 meq. sulfonate groups per 100 grams of sulfonated polymer, more preferably 7 to 40; and most preferably 7 to 20. The meq. of sulfonate groups per 100 grams of polymer is determined by both titration of the polymeric sulfonic acid and Dietert Sulfur analysis. In the titration of the sulfonated polymer, the polymer is dissolved in solvent consisting of 95 parts by volume of toluene and 5 parts by volume of methanol at a concentration level of 50 grams per liter of solvent. The sulfonated EPDM terpolymer is titrated with ethanolic sodium hydroxide to an Alizarin-Thymolphthalein end-point.

The sulfonated EPDM terpolymer is gel free and hydrolytically stable. Gel is measured by stirring a given weight of polymer in a solvent comprised of 95 vol-toluene-5 vol-methanol at a concentration of 5 wt. %, for 24 hours, allowing the mixture to settle, withdrawing a weighed sample of the supernatant solution and evaporating to dryness. Hydrolytically stable means that the acid function, in this case the unneutralized sulfonate groups, will not be eliminated under neutral or slightly basic conditions to a neutral moiety which is incapable of being converted to highly ionic functionality.

The sulfonated EPDM terpolymer is neutralised by the addition of a solution of a basic salt to the unneutralized sulfonated EPDM terpolymer dissolved in the mixture of the aliphatic alcohol and non-reactive solvent. The basic salt is dissolved in a binary solvent system consisting of water and/or an aliphatic alcohol. The counterion of the basic salt is a carboxylic acid having from 1 to 4 carbon atoms per molecule, a hydroxide, an alkoxide having about 1 to about 4 carbon atoms per molecule or a mixture thereof. The preferred neutralizing agent is a metal acetate, more preferably zinc acetate. Sufficient metal salt of the carboxylic acid is added to the solution of the acid form of the elastomeric polymer to effect neutralization. It is preferable to neutralize at least 95% of the unneutralized sulfonate groups, more preferably 98%, most preferably 100%. Examples of metal oxides useful in preparing metal sulfonates are MgO, CaO, BaO, ZnO, Ag_2O, PbO_2 and Pb_3O_4. Useful examples of metal hydroxides are NaOH, KOH, LiOH, $Mg(OH)_2$ and $Ba(OH)_2$. Alternatively, the unneutralized sulfonated groups of the unneutralized sulfonated EPDM terpolymer can be neutralized with an organic amine such as described in U.S. Patent 3,642,728.

The neutralized sulfonated EPDM terpolymer is incorporated into the hot melt adhesive composition at 5 to 100, more preferably about 10 to 90 and most preferably 15 to 75 parts by weight per 100 parts by weight of the highly unsaturated hydrocarbon rubber.

C. Plasticizers

The metal sulfonate containing polymers at higher sulfonate levels can possess extremely high melt viscosities and are thereby difficult to process. The optional addition of ionic group (preferential) plasticizers markedly reduces melt viscosity and frequently enhances physical properties. To the neutralized sulfonated EPDM terpolymer is

added, in either solution or to the crumb of the sulfonated EPDM terpolymer, a preferential plasticizer which is a carboxylic acid having 5 to 30 carbon atoms, more preferably 8 to 22 carbon atoms per molecule or a basic salt of these carboxylic acids, wherein the metal ion of the basic salt is aluminum, ammonium, lead or an ion of a metal of Groups IA, IIA, IB and IIB of the Periodic Table of Elements or a mixture thereof. The carboxylic acids may be lauric, myristic, palmitic or stearic acids or a mixture thereof; e.g., zinc stearate, magnesium stearate or zinc laurate.

The preferential plasticizer may be incorporated into the neutralized sulfonated EPDM terpolymer at 3 to 75, more preferably at 7 to 50, and most preferably at about 10 to 30 parts by weight based on 100 parts by weight of the neutralised sulphonated polymer.

The metallic salt of the carboxylic acid can also be used as neutralizing agent. In the case of the neutralizing agent and plasticizer being the identical chemical species, additional metallic salt is added over the required levels of neutralization. Alternative preferential plasticizers are amines, amides such as stearamide, ammonium and amine salts of carboxylic acids or mixtures thereof. The preferred plasticizers are carboxylic acids having about 8 to about 22 carbon atoms per molecule, metallic salts of these carboxylic acids or a mixture thereof. The resultant neutralized sulfonated elastomeric polymer with preferential plasticizer is isolated from the solution by conventional steam stripping and filtration.

D. Commercial Tackifier Resins

To the hot melt adhesive composition is added a commercial tackifying resin having a softening point of 0 to 160°C, more preferably 50 to 140°C and most preferably 70 to 120°C. A variety of

commercial tackifier resins are available. Some of these resins contain α and/or β pinene base polyterpene resins as the main ingredient while others are derived from the polymerization of petroleum or coal distillates which consist of aliphatic dienes, mono and di-olefins and cyclic olefins having 5 or 6 carbon atoms per molecule. The latter type of tackifiers have primarily piperylene and/or isoprene structure. A general but excellent description of tackifying resins derived from petroleun derivatives can be found in, for example, Encyclopedia of Polymer Science and Technology, Vol. 9, Pages 853 to 860, chapter by John Findlay, published by John Wiley & Sons, NY (1968).

Typical but non-limiting tradenames of these commercial tackifiers are Wingtak of Goodyear, Escorez of Exxon, Piccolyte of Hercules and Zonrez of Arizona Chemicals. Recently these and various other companies have also started marketing relatively higher softening point resins. These are generally modified aliphatic hydrocarbon resins and/or hydrogenated polycyclics. The physical appearance of these commercial tackifying resins varies, depending upon their softening point, they can be either viscous liquids or light-colored solids at room temperature. Most often their initial color (Gardner) is 3.0 to 7.0 and the density from 0.7 to 1.0 gm/cm^3 at room temperature. The acid number of these resins is usually less than 1. In general, the molecular weight of these commercial tackifying resins is not homogeneous, it spreads the number average molecular weight $\overline{Mn}$ can be from 300 to 5000 and more preferably 500 to 2000 and most preferably 700 to 1600.

As well-known to those familiar with the use of tackifying resins, because of their wide range compatability, any of them can be used with sulfonated polymers in proper formulation, which will yield adhesive systems of varying physical characteristics. To cite an example in the present invention, the tackifying resins used are those based on

hydrocarbon resins.

These hydrocarbon tackifier resins are incorporated into the hot melt adhesive composition at 25 to 200, more preferably 30 to 200, and most preferably 35 to 150 parts by weight per 100 parts by weight of the highly unsaturated hydrocarbon rubbers.

E. Method of Forming Blend Adhesive Composition

The blend compositions of the highly unsaturated hydrocarbon rubber, neutralized sulfonated elastomeric polymer with or without preferential plasticizer and the hydrocarbon tackifier resin can be formed by techniques well-known in the art. For example, the blend composition of the hot melt adhesive can be compounded on a hot two-roll mill. Other methods known in the art which are suitable for making these compositions include those methods employed in the plastic and elastomer industries for mixing polymer systems. An excellent polymer blend composition of this invention can be obtained through the use of a high shear batch intensive mixer called the Banbury. Alternatively, economic advantages in terms of time and laborsavings can be obtained through the use of a Farrel Continuous Mixer, a twin screw extruder, or tandem extrusion techniques which are continuous mixing types of equipment. The Banbury mixing device is the preferred batch-type mixer, and the twin screw extruder is the preferred continuous mixer.

F. Extended Blend Adhesive Composition

To the blend composition of the hot melt adhesive compositions can be added fillers which are talc, ground calcium carbonate, water precipitated calcium carbonate, delaminated, calcined or hydrated clay, silica, a carbon black, or a mixture thereof. These fillers are incorporated into the blend composition at 5 to 800, more preferably at 50 to 500; and most

preferably at 75 to 300 parts by weight per 100 parts by weight of the highly unsaturated hydrocarbon rubber. Typically, these fillers have a particle size of 0.03 to 20 microns, more preferably 0.3 to 10, and most preferably 0.5 to 10. The oil absorption as measured by grams of oil absorbed by 100 grams of filler is about 10 to 100, more preferably 10 to 85 and most preferably 10 to 75. Typical fillers employed in this invention are illustrated in Table I.

TABLE I

Filler	Code No	Oil Absorption grams of oil/ 100 grams of filler	Specific Gravity	Avg. Particle Size Micron	pH
Calcium Carbonate Ground	Atomite	15	2.71		9.3
Calcium Carbonate Precipitated	Purecal U	35	2.65	.03-.04	9.3
Delaminated Clay	Polyfil DL	30	2.61	4.5	6.5-7.5
Hydrated Clay	Suprex		2.6	2	4.0
Calcined Clay	Icecap K	50-55	2.63	1	5.0-6.0
Magnesium Silicate	Mistron Vapor	60-70	2.75	2	9.0-7.5

G. Oil Extended Adhesive Compositions

It is observed that the blend composition of the present invention can also include oils further to improve low temperature properties and tack characteristics of the resulting adhesive. Levels of oil of 1 to 100 parts by weight per 100 parts of the highly unsaturated hydrocarbon rubber can be incorporated, more preferably 1 to 90 parts. Oils are particularly useful when high levels of petroleum resin tackifiers are used since such materials can harden the resulting composition. Oils can further soften and reduce the cost. Typical oils that can be used may be low viscosity aromatic, naphthenic or paraffin petroleum oils, having less than 2 wt. % polar type compounds. Typical oils are illustrated in Table II.

TABLE II

Type Oil	Oil Code No	Viscosity ssu	M_n	% Polars	% Aromatic	% Saturates
Paraffinic	Sunpar 115	155	400	0.3	12.7	87.0
Paraffinic	Sunpar 180	750	570	0.7	17.0	82.3
Paraffinic	Sunpar 2280	2907	720	1.5	22.0	76.5
Aromatic	Flexon 340	120	-	1.3	70.3	28.4
Naphthenic	Flexon 765	505	-	0.9	20.8	78.3

H. Method of Fabrication of Adhesive Compositions

Because of the significant advances in the packaging technology, the hot melt adhesive compositions can be used by conventional polymer fabricating techniques. After the blending is complete, the adhesive mass can either be extruded and/or calendered to a uniform thickness on top of the substrate which could be paper, cloth, aluminum foil or glass fabric. The temperature and throughput of the extrusion are variable depending upon the viscosity of the tackifying mass and the desired coating thickness. Typically the temperature of extrusions and rolls may be from about 200° to 400°F. The substrates or backings to which the pressure sensitive adhesive compositions are applied may be of various porous or nonporous types and they may be organic or inorganic in nature. Most generally, these materials are those which are customarily employed in pressure sensitive tapes, either the cloth or paper backed types or tape backings made of synthetic materials, for example, polyesters such as the copolymer of ethylene glycol with terephthalic acid, vinyls such as a copolymer of vinylidene chloride and vinyl chloride, or a copolymer of vinylidene chloride with acrylonitrile, cellophane, cellulose acetate, polyvinyl chloride, polyvinyl acetate, polypropylene, polyethylene, ethylene-propylene plastic copolymer. Sheetings and tapes of cloth or textiles of either natural or synthetic fiber origin, such as glass fiber cloth, wood and finally sheets or strips of metals such as steel, copper, aluminum, and alloys thereof can also be employed. In general, the backings employed are those which have heretofore been conventionally employed in preparing pressure sensitive labels, tapes, sheetings and the like and the selection of any particular substrate material is not a specific novel feature of the present invention.

The advantages of the hot melt adhesive compositions of the present invention can be more readily

appreciated by reference to the following examples and tables. Unless otherwise specified, all measurements are in parts per hundred by weight.

Example I

Five hundred grams of an EPDM terpolymer (MD-76-5) was dissolved under agitation in 5000 ml. of n-hexane at about 40°C. After all this polymer was dissolved, the solution was cooled to low temperature and 17.22 ml. of active anhydride (182.25 mmoles) was added. After that, while stirring the mixture 6.31 cc of 95% H_2SO_4 (11.50 mmol) was added dropwise, the stirring of the solution was continued for an additional 30 minutes for the sulfonation reaction to complete. After this period, the sulfonation reaction was inactivated by adding 28.63 gm of zinc acetate dissolved in 400/20 ml. mixture of CH_3OH/H_2O. Antioxidant 2246 (2.5 gm) was then added to the cement and stirring was continued for an additional 30 minutes. The resultant neutralized sulfonated EPDM terpolymer was isolated by steam stripping. It was then washed with distilled water and pulverized with water in a Waring Blender, followed by filtering by a rubber drum. The final drying of the polymer was done in an aromatic dryer at 100°C.

The sample is identified as neutralized sulfonated EPDM terpolymer 1-1.

The preparation technique of a sulfonated EPDM terpolymer Zn salt having 15 meq. sulfonate groups (Samples 1-2) were the same as above of Sample 1-1. The only difference was in the amount of various chemical ingredients required for the sulfonation and neutralization reaction. The amount of acetic anhydride used (for Sample 1-2) was 13.40 ml (141.75 mmoles), H_2SO_4 4.91 cc (87.50 mmoles) and zinc acetate 23.05 gms.

The sulfur analysis on Samples 1-1 and 1-2 was done by Dietert Sulfur analysis and these polymers were found to have sulfonate groups of 20 meq. and 15 meq. per 100 gm of sulfonated polymer.

Example 2

The neutralized sulfonated EPDM terpolymers of Example 1 (1-1 and 1-2), polyisoprene and a tackifier resin such as Wingtak Plus or Escorez 1310 were dry blended in the proportion as indicated in Table III and subsequently mixed into a homogenous blend on a hot two roll mill at about 150°C for about 15 minutes. Blends 2-6, 2-7, 2-8 and 2-9 additionally include ionic preferential plasticizer. Blend 2-5 is a presently used commercial formulation for hot melt adhesive compositions.

Conclusions

Table IV illustrates various qualitative and quantitative properties of these blends. It can be readily noted that the blends incorporating the sulfonated polymers, Blends 2-1 and 2-2, are not only very tacky but have relatively good green strength. The strength of such materials can be controlled by the proper changes in the formulations and/or by adding the preferential plasticizers. Thus, for example, samples 2-6 and 2-7 are not only very tacky but have extremely high green strength. Such systems are excellent for various pressure sensitive adhesive applications, especially as hot melt adhesives. Because of their high green strength, these materials will undergo very little creep deformations and thus their shelf use life can be expected to be significantly better over those conventional adhesives. In accordance with their high strength, their high temperature properties will also be improved, and thus for example, laminates prepared using such adhesives will not be expected to distort due to flow or failure if subjected to sudden temperature or pressure changes.

Some quantitative numbers on the peel strength of these blends are listed in the fifth column of Table IV.

TABLE III

Blends of Polymers with Petroleum Resins

Blend No	Parts by Weight								
	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8	2-9
Polyisoprene	42.5	47.0	42.5	42.5	----	35.0	35.0	20.0	15.0
Sulfo EPDM Zn Salt (~20 meq.)	7.5	3.0	----	----	----	15.0	15.0	10.0	5.0
Sulfo EPDM Zn Salt (~15 meq.)	----	----	7.5	7.5	----	----	----	----	----
Kraton 1107 *	----	----	----	----	50.0	----	----	----	----
Wingtak Plus	50.0	50.0	50.0	----	50.0	50.0	50.0	70.0	80.0
Escorez 1310	----	----	----	50.0	----	----	----	----	----
Zinc Stearate	----	----	----	----	----	3.0	----	----	----
Stearic Acid	----	----	----	----	----	----	2.0	2.0	1.0

*Kraton 1107 is a block copolymer of the structure ABA in which A is a block of styrene (total ~15% by weight) whose number average molecular weight is in the range of 10,000 to 30,000. B is an elastic block of isoprene (~85%) having a number average molecular weight of about 100,000.

TABLE IV

Blend No	Green Strength	Tackiness	Clarity	Peel Strength Pound-Force
2-1	Medium	Very Tacky	Clear	0.6
2-2	Medium	Very Tacky	Clear	1.5
2-3	Medium	Tacky	Light Yellow	2.7
2-4	Medium	Tacky	Light Yellow	2.0
2-5	High	Tacky	Clear	11.9
2-6	Very High	Very Tacky	Light Yellow	1.7
2-7	Very High	Very Tacky	Light Yellow	2.8
2-8	High	Tacky	Light Yellow	10.2
2-9	High	Slightly Tacky	Clear	10.3

The peel strength values were obtained by a method similar to ASTM D-429 adhesion test. In brief, the samples were sandwiched between mylar sheets and pressed to a thickness of about 25 mils using a hot press. Rectangular strips of 1/2" width and 3" long were cut and 90° peel tests were performed on an Instron at room temperature. The resin free sections of the mylar film were clamped into air jaws to avoid any slippage during pulling. The samples were pulled at 5"/min. crosshead speed. The force and elongation of the samples were recorded on a strip recorder. The force necessary to separate the mylar sheets was taken as the peel strength of the blend. The initial peak values are reported in the fifth column of Table IV.

CLAIMS

1. A hot melt adhesive composition which comprises:

(a) a highly unsaturated hydrocarbon rubber or neoprene;

(b) about 5 to about 100 parts by weight of a neutralised sulphonated EPDM terpolymer per 100 parts by weight of said highly unsaturated hydrocarbon rubber or neoprene, said neutralised sulphonated EPDM terpolymer having about 5 to 50 meq. of neutralised sulphonated groups per 100 grams of said neutralised sulphonated EPDM terpolymer; and

(c) about 25 to about 200 parts by weight of a hydrocarbon resin of a petroleum or coal tar distillate per 100 parts by weight of said highly unsaturated hydrocarbon rubber or neoprene.

2. A composition according to claim 1 wherein said highly unsaturated hydrocarbon rubber is polyisoprene.

3. A composition according to either of claims 1 and 2 wherein said EPDM terpolymer consists of about 40 to about 65 wt. % of ethylene, of about 25 to about 53 wt. % of propylene and of about 2 to about 10 wt. % of a nonconjugated diene.

4. A hot melt adhesive composition according to claim 3 wherein said nonconjugated diene is 5-ethylidene-2-norbornene.

5. A composition according to any one of the preceding claims wherein the neutralised sulphonate groups are neutralised with a counterion selected from ammonium, aluminum, antimony, iron, lead and Groups IA, IIA, IB and IIB of the Periodic Table of Elements.

6. A composition according to any one of the preceding claims which includes about 3 to about 75 parts by weight of an ionic preferential plasticizer per 100 parts by weight of said neutralised sulphonated EPDM terpolymer, wherein said preferential plasticizer is a carboxylic acid having about 8 to about 22 carbon atoms per molecule, a metallic salt of said carboxylic acid, an amides having an aliphatic group of about 8 to about 22 carbon atoms, an amine, a urea, a thiourea or a mixture thereof.

7. A composition according to any one of the preceding claims which includes about 5 to about 800 parts by weight of a filler per 100 parts by weight of said highly unsaturated hydrocarbon resin, said filler being calcium carbonate, silica, a carbon black, a clay, talc or a mixture thereof and/or less than about 100 parts by weight of an oil having less than 2 wt. % polars per 100 parts by weight of said highly unsaturated hydrocarbon resin or neoprene.

8. A composition according to any one of the preceding claims wherein said hydrocarbon is derived from the polymerisation of petroleum or coal distillates which consist of aliphatic dienes, mono- and di-olefins and cyclic olefins having 5 or 6 carbon atoms per molecule.

9. A composition according to any one of the preceding claims which includes from about 1 to about 100 parts by weight of an oil per 100 parts by weight of said highly unsaturated hydrocarbon resin, said oil being an aromatic, naphthenic or paraffinic basestock.

European Patent Office

EUROPEAN SEARCH REPORT

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Application number

EP 81304786.7

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.³)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
	No relevant documents have been disclosed.		C 09 J 3/12 C 09 J 3/14 C 08 L 9/00 C 08 L 23/16 C 08 L 57/02 C 08 L 91/00 C 08 K 5/09
			TECHNICAL FIELDS SEARCHED (Int. Cl.³) C 09 J C 08 L

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	01-12-1981	KAHOVEC

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